EPA Region 10 SOP For the Validation of of Method 1668 Toxic, Dioxin-like, PCB Data

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The Quality Assurance Unit of EPA Region 10 has developed the following guidelines which should be used to access the quality of toxic, dioxin-like PCB data from samples originating from Region 10 sampling sites. This SOP is based upon the data validation principles specified in National Functional Guidelines For Organic Data Review, December, 1990, and the quality control (QC) requirements of EPA Method 1668, Draft Revision, 10/4/95. The validator of toxic, dioxin-like PCB data should obtain a copy of the site-specific Quality Assurance Project Plan (QAPP) and use the Data Quality Objectives and QA requirements of the QAPP to assess the data. This SOP requires that the following criteria be evaluated when determining the quality of toxic, dioxin-like PCB data:

1.0 HOLDING TIME AND PRESERVATION OF SAMPLES

1.1 Objective. To determine the validity of the measurement results based upon EPA requirements for preservation and holding time of the samples from day of collection to day of extraction. EPA also has holding time requirements for extracts which is the time from extraction of the samples to injection of the sample extracts.

1.2 Criteria. Holding time and preservation requirements for the measurement of PCBs as Aroclors in water samples under the CWA (40CFR Part 136), SDWA, and RCRA have been promulgated and codified under 40CFR. These regulations require that water samples be preserved by cooling to 4°C using a holding time of 7 days from day of collection to day of extraction of the sample. In addition, the maximum holding time of extracts is 40 days from day of extraction to day of injection of the extract.

The holding time and preservation requirements of toxic, dioxin-like PCB isomers in non-water matrixes have not been promulgated by EPA. Therefore, the data validator should use the holding time specified in the EPA approved site-specific Quality Assurance Project Plan (QAPP).

Method 1668, Draft Revision, 10/4/95 recommends different preservation and holding times for PCB congeners. Consult Section 8.0 of Method 1668 for preservation and holding time recommendations.

Section 8.2 states that aqueous samples should be tested for chlorine residual. If chlorine is present, 80mg of sodium thiosulfate should be added per liter of water. Adjust pH to 2-3 with sulfuric acid. Store samples in dark at 0 to 4°C. Method 1668 recommends a holding time of less that one year.

Section 8.3 states that solid, semi-solid, oily, and mixed phase samples should be stored in wide mouth bottle at <4°C. Section 8.3 states that solid, semi-solid, oily, and mixed phase samples should be stored in the laboratory at < -10°C. Method 1668 recommends a holding time of less that one year.

Section 8.4 states that fish and tissue samples should be wrapped in aluminum foil, cooled to <4°C, and shipped to lab. Upon receipt at the lab, tissue samples should be stored in the dark at < -10°C. Method 1668 has recommended a holding time of one year for tissue samples which are frozen at < -10°C. Once frozen tissue samples are thawed, tissue samples must be extracted within 24 hours.

Extracts should be analyzed within 40 days of extraction.

1.3 Action. If **40CFR Part 136** and the QAPP for the samples do not specify a holding time, then the holding time which is recommended by applicable EPA method -- Method 1668 should be used. Whenever samples or extracts are analyzed after holding time expiration date, the results should be considered to be minimum concentrations and must be qualified with a "J3". Samples which are not preserved correctly should be qualified with a "J" flag.

2.0 GC/MS PERFORMANCE CHECK

2.1 Objective. Gas chromatograph/mass spectrometer (GC/MS) instrument performance checks stated in Method 1668 Section 10.0 are performed to ensure mass resolution, identification, and calibration. Conformance is determined using standard materials, therefore, these criteria should be met in all circumstances.

2.2 Criteria. For the PFK molecular leak, the resolution must be greater than or equal to 10,000. The deviation between the exact mass and the theoretical mass for each of the three to five ions monitored must be less than 5 ppm. If the mass spectrometer is adjusted the resolution must be tested again and the resolution documented.

The mass spectrometer shall be operated in a mass-drift correction mode using PFK to provide lock-masses. Each lock-mass shall be monitored and shall meet the QC requirements of Section 7.1 of Method 1668.

Ion abundance ratios. All labeled and unlabeled PCB congeners in the CS1 standard shall be within the QC limits described in Section 10.2 and in Table 9 for their respective ion abundance ratios.

The HRGC/HRMS must meet the minimum levels in 1668 Table 2. All labeled and unlabeled analytes in the CS1 calibration standard must have signal to noise ratios greater than or equal to 10.0. (see Method 1668/Section 10.2)

The absolute retention time of PCB 169 shall exceed 20.0 minutes on the SPM-Octyl column, and the retention time of PCB 157 shall exceed 25.0 minutes on the DB-1 column. (see Method 1668/Section 10.2.4)

The compound pairs in the window defining mixtures shall be determined. (see Method 1668/Section 10.3)

The isomer specificity requirements stated in Method 1668 Section 10.4 shall be met.

2.3 Action. Failure to meet either the resolution or the retention window criteria invalidates all calibration or sample data collected during the 12 hour time window.

3.0 INITIAL CALIBRATION

3.1 Objective. Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for PCBs. Initial calibration demonstrates that the instrument is capable of producing a linear calibration curve.

3.2 Criteria. There shall be an initial calibration curve consisting of five points for each analyte. The initial calibration curve shall be determined less than 30 days from the time the first samples of a Sample Delivery Group (SDG) are measured by the lab. The lab shall use the same calibration standards with the same lot number, for all internal standards, and labeled standards used in measuring the initial calibration curve, verification standards, field samples, and method blanks on both the primary GC column and on the secondary confirmation GC column. If an analyte is calculated by the isotope dilution method, an averaged response factor may be used if the RSD is less than 20% For analytes calculated by the internal standard method, an averaged response factor may be used if the RSD is less than 35%. Otherwise, for either calculation method, the complete curve must be used (see Method 1668/Sections 10.5 and 10.6).

3.3 Action. If the Initial Calibration Curve is older that 30 days, or if internal standards or labeled standards used in measuring of the initial calibration curve, verification standards, field samples, and method blanks on both the primary GC column and on the secondary confirmation GC column or not from the same lot number, then all measurement data should be qualified with a "J" qualifier.

If the RSD exceeds 20% for those analytes analyzed by isotope dilution or 35% for those analytes analyzed by the internal standard method, qualify positive results with "J", and non-detected analytes using professional judgement. At the reviewer's discretion, a more in-depth review may be conducted to minimize data qualification by examining the entire curve and the quantitation method used.

4.0 CALIBRATION VERIFICATION MEASUREMENTS

4.1 Objective. Compliance requirements for satisfactory instrument calibration are established to ensure that the

instrument remains capable of producing acceptable qualitative and quantitative data each day that samples are measured.

4.2 Criteria. Native and labeled PCB congeners in the calibration verification standard (CS3) and in the Ongoing Precision and Recovery Standard (OPR) shall meet the acceptance criteria which are specified in Method 1668, Section 15.0.

4.3 Action. The reviewer should use professional judgement to determine if it is necessary to qualify the data. The following are guidelines:

> If the %D for an analyte is outside the acceptance window, qualify positive results "J" and non-detected "UJ" for that analyte. If the ion abundance criteria are not met results qualify all results for that analyte "R".

5.0 SYSTEM PERFORMANCE

5.1 Objective. The performance of the method by the Laboratory is examined by determination of the Laboratory's ability to perform the method (Initial Precision and Recovery (IPR) study) and to demonstrate the Laboratory's continuing ability to perform the analysis. See Section 9.0 of Method 1668, Draft Revision, 10/4/95 for initial and ongoing QA and QC requirements.

As part of measuring system performance, Method 1668 require that samples and standards be measured within require QC limits. QC criteria such as required relative retention times of labeled and native isomers, theoretical ion abundance ratios, recovery limits for OPR and VER standards, and recovery limits for spiked labeled target compounds must be met in order to demonstrate that the measurement system is within the specified control limits of Method 1668. In addition, all samples will be spiked with the labeled compound spiking solution described in Section 7.10.3.

5.2 Criteria. Initial precision and accuracy (IPR). All cleanup steps used in processing samples shall be included in the IPR study. All analytes shall be within the IPR limits in Table 6 of Method 1668 (use Table 6a if only PCBs 77, 126, and 169 are determined). There will be one PAR sample for each sample set analyzed. The recovery of labeled spiked isomers in samples shall be within the QC limits specified in Table 7 (use Table 7a if only PCBs 77, 126, and 169 are measured).

QC limits such as required relative retention times of labeled and native isomers, theoretical ion abundance ratios, recovery limits for OPR and VER standards, and recovery limits for spiked labeled target compounds must be within control limits of Method 1668.

5.3 Action. Results for analytes which do not meet either IPR or PAR requirements should be qualified with either "J" or "UJ". If an analyte is not recovered for an PAR sample, results must be qualified with an "R" for that analyte. Failure to meet QC limits of the method may result in measurement values which are qualified with a "J" or "UJ". In specific cases where major QC limits are exceeded, the data validator may determine that the measurement system is out of control, which would require that all measurement results for a sample be qualified with a "J", "UJ", or "R" flag.

6.0 METHOD BLANKS

6.1 Objective. To determine the existence and magnitude of contamination of samples resulting from laboratory activities. The criteria for evaluation of blanks will apply to any blank associated with the samples, including any method blanks, instrument blanks, field equipment blanks, transfer blanks, trip blanks, or solvent blanks.

6.2 Criteria.

1. The criteria for the frequency of extraction and analysis of method blanks as stated in Section 9.5 of Method 1668 shall be followed and demonstrated in the documented data. The maximum amount of toxic, dioxin-like PCB isomer contamination in method blanks is stated in Table 2 of Method 1668.

2. A method blank must be measured on each GC/MS system which is used to measure a group of samples. This requirement includes measuring method blanks for PCBs 156 and 157 on the secondary GC confirmation column (DB-1) if PCBs 156 and 157 are detected on the primary GC column, SPB-Octyl (see GC confirmation requirements in Method 1668, Section 16.5).

6.3 Action. If the maximum contamination requirements of specific PCB congeners stated in Table 2 of Method 1668 are not

met, then all isomers in all samples associated with a method blanks shall be qualified with a "J1" flag. If the frequency of measuring method blanks is not met by the laboratory in the data submitted, then the results of all samples which do not meet the frequency of extraction and measurement of method blanks shall be qualified with a "R" flag. Any measurement of PCB congeners in a sample that is also measured in any associated blank, is qualified with a "U" flag if the sample concentration is less than 5 times the blank concentration.

7.0 RECOVERY OF SPIKED C-13 LABELED PCB CONGENERS

7.1 Objective. Labeled PCB congeners are added to each sample and method blank prior to extraction. The role of these C-13 labeled spiked compounds is to be an internal standard for the quantitation of native toxic, dioxin-like PCB isomers, and to serve as surrogates for the assessment of method performance in the sample matrix.

7.2 Criteria. The recovery of each C-13 labeled toxic, dioxin-like PCB isomer using Method 1668 must be within recovery limits specified in Table 7 (see Table 7a if PCBs 77, 126, and 169, only, are measured).

7.3 Action. If any of the labeled percent recoveries are outside the guideline windows for individual analytes listed in Table 7 (see Table 7a if PCBs 77, 126, and 169, only, are measured), the individual isomer for that sample will be qualified with a "J" flag. For non-detected toxic, dioxin-like PCB compounds whose percent recoveries are outside the guideline windows for individual analytes, these will be qualified with a "UJ" flag.

8.0 RECOVERY OF C-13 LABELED INTERNAL STANDARDS

8.1 Objective. The purpose of adding four labeled internal standards (see Method 1668, Section 7.12) prior to injecting sample extracts and standards into the GC/MS is to determine the recovery efficiency of the extraction and cleanup procedures, to determine if the GC/MS sensitivity and response are stable during every analytical run, and to determine if the same amount of extract was injected into the GC/MS.

8.2 Criteria. The sum of the area counts of two masses for each of the two cleanup standards for samples, blanks, and standards must not vary by more than a factor of four (-25% to +200%) from the sum of the associated average areas from the five initial calibration standards.

8.3 Action. The reviewer should use professional judgement to determine if it is necessary to qualify the data. The following are guidelines:

1. If the sum of the two quantitation area counts of each internal standard in samples or blanks are outside a -25% to +200% window which is determined by averaging the sum of the area counts present in the five initial calibration standards, then positive measurement results for native compounds should be qualified with a "J".

2. If the sum of the two quantitation area counts is greater that 200%, then non-detected compounds should not be qualified.

3. If the sum of the two area counts is less than 25%, then non-detect compounds should be qualified with a "UJ".

4. If the sum of the area counts is less than 10%, then non-detect target compounds should be qualified with a "R".

9.0 PROJECT AND REGIONAL QUALITY ASSURANCE SAMPLES

9.1 Objective: The data validator should consider the data of samples which are identified as field duplicates, transfer blanks, trip blanks, blind spikes, blind blanks, and performance evaluation (PE) samples.

9.2 Criteria. If QA samples are included among the field samples for measurement by the laboratory, then the data validator should refer to the applicable QAPP for any QA requirements regarding QA samples. Results from the measurement of project and regional QA samples will reflect upon the ability of the laboratory to report analytical results of known and documented quality which meet the PARCC requirements of the QAPP.

9.3 Action. The data validator should recommend action in accordance with Regional specifications, QAPP specifications, or criteria for acceptable PE sample results. Poor performance by

the laboratory on blind PE samples may indicate that the laboratory analytical system is out of control, or that the amount of toxic, dioxin-like PCB isomers reported by the laboratory is an estimated quantity. The data validator should use her/his professional judgement to assess if "J" or "R" qualifiers should be placed upon the data due to the measurement of QA or PE samples.

10.0 COMPOUND IDENTIFICATION

10.1 Objective. The qualitative criteria for target compound identification have been established by EPA Method 1668 to minimize the number of erroneous identifications. An erroneous identification can be either a false-positive (reporting a target compound when it is not present in the sample), or false-negative (not reporting a compound that is present in the sample). The addition of single or double blind PE samples among field samples provides ancillary data to support the laboratory's ability to meet QAPP objectives.

10.2 Criteria. EPA Method 1668 specifies certain requirements and guidelines for the positive identification of certain toxic, dioxin-like PCB isomers such as PCBs 156 and 157 (see Section 16.5). The most frequently encountered interfering compounds to the measurement of toxic, dioxin-like PCB isomers are chlorinated substances such as other PCB congeners, Polychlorinated dioxins and furans (PCDDs/PCDFs), methoxy biphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides that may be found at concentrations several orders of magnitude higher than the analytes of interest. Method 1668 requires that if certain PCB congeners such as PCB 156 and 157 are measured on the primary GC column, SPB-Octyl, that PCBs 156 and 157 must be confirmed using second dissimilar GC column (DB-1) before specific identifications can be made.

In this part of the SOP for the validation of toxic, dioxin-like PCB data, the qualitative identification criteria specified in Method 1668, Section 16.0 must be met for a GC peak to be identified as a PCB congener:

1. The signals for the two exact m/z's listed in Table 8 must be present, and must maximize within plus or minus 2 seconds of one another (see 1668/Section 16.1).

2. The signal-to-noise ratio (S/N) of each of the two exact m/z's must be greater than or equal to 2.5 for a sample

extract, and greater than or equal to 10 for a calibration standard (see 1668/Section 16.2).

3. The ratio of the integrated ion currents (EICPs) of both the exact m/z's monitored must be within the limits which are listed in Table 9 of the method (see 1668/Section 16.3).

4. The relative retention time (RRT) of the peaks representing a unlabeled PCB congener must be within 5% of the limits listed in Table 2 (see Method 1668, Section 16.4).

5. The measurement of PCBs 156 and 157 on the primary SPD-Octyl GC column must be confirmed by analysis on a confirmatory column such as DB-1. All QC requirements of the method must be met on both the primary and secondary GC columns (see 1668/Section 16.5).

10.3 Action. The validator of the data must use his/her professional judgement in evaluating the data using the above identification criteria. Generally, if all of the above criteria for the identification of toxic, dioxin-like PCB isomers are not met, then each reported positive measurement of a PCB congener should be considered a non-detect, and therefore flagged with a "R" flag. The "R" flag in this case is based upon the fact that the presence of the isomer in the sample can not be corroborated by the laboratory data.

11.0 LABORATORY CONTACTS

Provide and attached to the validation memo a copy of all telephone logs and correspondence with the laboratory concerning the quality of data submitted by the laboratory.

12.0 OVERALL ASSESSMENT OF THE QUALITY OF THE DATA

12.1 Objective. The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments of the quality of the data. The overall assessment of the data should be made after the data validator considers the DQOs and other QA requirements of the site-specific QAPP. It should be noted that the data reviewer does not determine or report the useability of the data. This determination is made by the Site Manager and by the other users of the data.

12.2 Criteria. The criteria for overall assessment is the QA and DQO criteria of the QAPP and the criteria listed above in this data validation SOP.

12.3 Action. Use professional judgement to determine if there is a need to further qualify the data. Write a brief narrative to give the user an indication of any analytical limitations of the data. Note if there are any inconsistencies observed between the raw data and the laboratory reported sample results.

DATA QUALIFIER DEFINITIONS

U - The analyte was analyzed for, but was not detected above the sample quantitation limit. The associated numerical value indicates the approximate concentration necessary to detect the analyte in this sample.

If a decision requires quantitation of the analyte below the associated numerical level, reanalysis or alternative analytical methods should be considered.

J - The analyte was analyzed for and was positively identified, but the associated numerical value may not be consistent with the amount actually present in the environmental sample.

A subscript may be appended to the "J" that indicates which of the following quality control criteria were not met:

J1 Blank Contamination: indicates possible high bias and/or false positives.

J2 Calibration range exceeded: indicates possible low bias.

J3 Holding times not met: indicates low bias for most analytes.

J4 Other QC parameter outside control limits: bias not readily determined.

J5 Other QC parameter outside control limits. The reported results appear to be biased high. The actual value of target compound in the sample may be lower than the value reported by the laboratory.

J6 Other QC parameter outside control limits. The reported results appear to be biased low. The actual value of target compound in the sample may be higher than the value reported by the laboratory.

R - The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet critical quality control criteria. The presence or absence of the analyte cannot be verified.

Resampling and reanalysis are necessary to confirm or deny the presence of the analyte.

UJ - The analyte was analyzed for and was not detected above the reported quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in this sample.

If a decision requires quantitation of the analyte close to the associated numerical level, reanalysis or alternative analytical methods should be considered.